

VINYL POLYMERIZATION

XI. Binary Systems of Poly (Methyl Methacrylate)/and Poly (Ethyl Methacrylate)/Solvent by Phase Separation

BY S. PADMA VASUDEVAN* AND M. SANTAPPA, F.A.Sc.

(Department of Physical Chemistry, University of Madras, Madras-25, India)

Received October 18, 1969

ABSTRACT

The thermodynamic interaction parameters of the systems, poly (ethyl methacrylate) / *n*-butanol and poly (methyl methacrylate) / *n*-butyl bromide and poly (methyl methacrylate) / isoamyl acetate were determined by methods involving phase separation and compared critically with values obtained by other methods. The validity of some of the well-known theoretical equations in the region of phase separation is considered.

INTRODUCTION

BINARY systems of a high polymer and solvent have been studied for the evaluation of thermodynamic parameters^{1, 2} and for checking the validity of various theoretical equations pertaining to thermodynamic properties of high polymer systems in the region of phase separation. Flory³ related the critical solution temperature, T_c , of the binary systems to the molecular weight of the polymer and evaluated the entropy parameter ψ and the θ temperature. This method was widely used⁴ for the evaluation of θ . But the values of ψ by this method are known⁵ to be higher than those estimated for the same systems by viscometry or osmometry. It has also been noted³ that the theoretical curves of the precipitation temperature (T_p) versus volume fraction (v_2) of the polymer, based on the Flory-Huggins' equation, were sharper than the experimental curves and the theoretical critical volume fractions were lower than the experimental. Subsequent workers⁶⁻¹¹ have indicated that the reason for this discrepancy lies in the assumption that the thermodynamic parameters are independent of concentration. Notably Maron^{9, 12} considered the dependency of Flory's parameter χ on volume fraction of the polymer and obtained better agreement between the theoretical and experimental curves. Recently, Elias^{13, 14} reported a quick method of estimation of θ compositions of nonsolvent-solvent systems by plotting the logarithm of volume fraction of

* Present address: Department of Chemistry, I.I.T., New Delhi.

the nonsolvent *versus* the logarithm of concentration of the polymer. Based on certain theoretical calculations, Cornet and Ballegooijen¹⁵ showed that a plot of theoretical χ (corrected for its concentration dependence) against $\log v_2$ was linear in the region $\log v_2 = -2$ to -5 and that $\chi = 0.5$ at $\log v_2 = 0$, a condition corresponding to the θ temperature. Thus a plot of $\log v_2$ *versus* $1/T_p$ in the region indicated would yield θ . In this paper, the thermodynamic parameters θ and ψ , evaluated by phase separation studies of binary systems of poly (ethyl methacrylate)/*n*-butanol, poly (methyl methacrylate) *n*-butyl bromide and poly (methyl methacrylate)/isoamyl acetate, are reported and compared with the values obtained by other methods such as viscometry. θ temperatures were evaluated by Flory-Huggins' as well as by Cornet-Ballegooijen's plots and compared. Also an attempt has been made to apply the Flory-Huggins' and Maron's theories to our data. The theoretical T_p *versus* v_2 curves were calculated based on Flory-Huggin's theory by the usual procedure.³ In the absence of separate osmometric and light scattering data for the estimation of temperature dependence of χ , Maron's theory was applied to give only a rough estimate of the parameters μ^0 and σ^0 .

EXPERIMENTAL

The polymers poly (M.M.A) and poly (E.M.A.) were prepared by solution polymerization of the corresponding monomers (Rohm and Hass, USA) in benzene at 60° C, using benzoyl peroxide as the initiator. The conversion was restricted to ~15% to avoid any branching. The molecular weight ranged from 10⁵ to 10⁶. The heterogeneous polymer samples were fractionated by standard procedure using benzene as the solvent and *n*-hexane as the nonsolvent. About 6–10 gm. of the polymer was fractionated to 20–30 fractions (0.1–0.4 gm. each fraction). The molecular weights of poly (E.M.A.) fractions were determined by viscometry in methyl ethyl ketone at 23° C using the relation due to Chinai *et al.*¹⁶

$$[\eta] = 2.83 \times 10^{-5} \cdot \bar{M}_w^{0.79}.$$

The molecular weights of poly (M.M.A.) fractions were determined from $[\eta]$ values in benzene at 30° C, using the relation due to Cohn *et al.*¹⁷:

$$= 5.2 \times 10^{-5} \cdot \bar{M}_w^{0.76} \text{ for } M_w \geq 35,000$$

$$= 19.5 \times 10^{-4} \cdot \bar{M}_w^{0.41} \text{ for } M_w \leq 35,000.$$

The solvents, benzene (S. Merck, AnalaR), methyl ethyl ketone (B.D.H. L.R. distilled), isoamylacetate (B.D.H. L.R. and M and B AnalaR, distilled),

n-butyl bromide (Riedel sample, AnalaR) and *n*-butanol (B.D.H. AnalaR) were purified by standard procedures and freshly distilled before use. The precipitation temperatures, T_p , were determined for different concentrations of polymer solutions (0–2%) expressed in terms of the volume fraction of the polymer v_2 (0.0–0.2). The apparatus used was a modification of the one used earlier by Shultz and Flory.¹ Assuming that there is no change in the total volume on mixing the polymer and the solvent, and taking the specific volume of the polymer to be equal to that of the liquid polymer, the volume fraction v_2 was calculated. The T_p values for more dilute solutions were obtained in a similar manner after adding the required amount of solvent through the glass tube. The T_p values were determined twice or thrice at each concentration to check the reproducibility. The intrinsic viscosities of various fractions of the polymer in these solvents were determined at different temperatures using an Ubbelohde viscometer.¹⁹

RESULTS

In Fig. 1 T_p versus v_2 curves for the system poly (E.M.A)/*n*-butanol is shown for fractions⁷ (mol. wt. = 7.261×10^5); Fr. 10 ($M = 5.834 \times 10^5$);

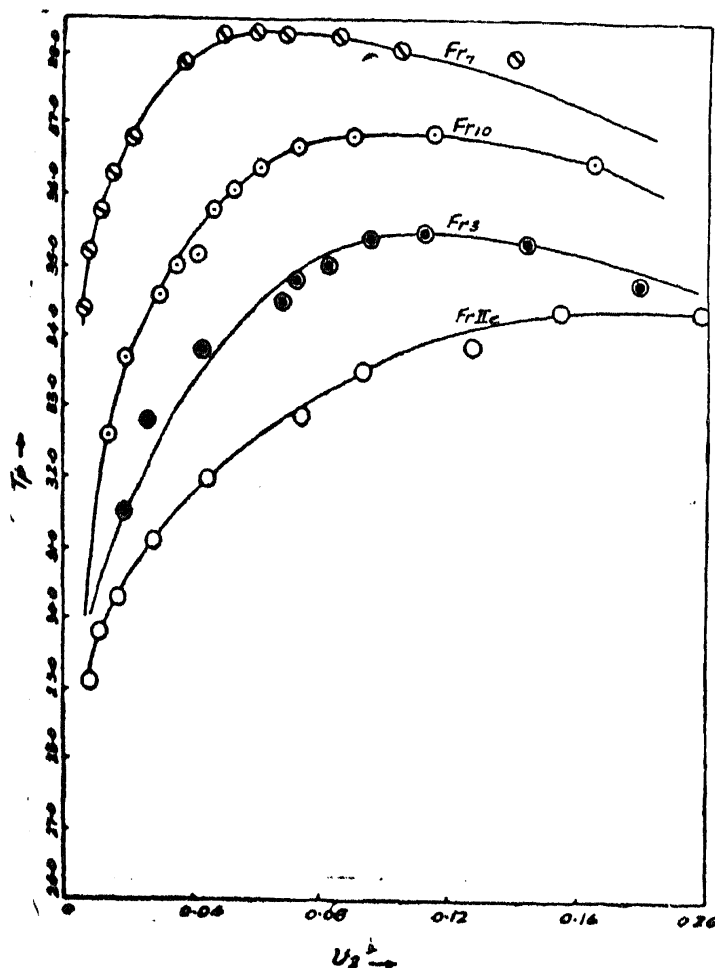


FIG. 1. T_p versus v_2 for poly (E.M.A)/*n*-butanol (Fr. 7, $M = 7.261 \times 10^5$; Fr. 10, 5.834×10^5 ; Fr. 3, 3.972×10^5 ; Fr. II e, 2.793×10^5).

Fr. 3 ($M = 3.972 \times 10^5$) and Fr. IIe ($M = 2.793 \times 10^5$). Similar curves with flat maxima were obtained for poly (M.M.A.)/*n*-butyl bromide (Fig. 2) and poly (M.M.A.)/isoamyl acetate systems (Fig. 3) for various fractions of the polymer. The dashed lines in Fig. 2 indicate theoretical curves based on the Flory-Huggins' theory. Plots of $1/T_p$ versus $1/x^2 + 1/2x$ for the various systems were linear [Fig. 4 typical for poly (E.M.A)/*n*-butanol]. Linear plots were obtained when $-\log v_2$ was plotted against $1/T_p$ and the θ temperatures were read off from the intercepts of such plots (Fig. 5). In Table I are listed the values of θ and ψ for the systems obtained by phase separation studies, along with the values obtained for the same systems by viscometry.

TABLE I
Values of θ , ψ and k obtained by precipitation

System	θ° K.			ψ		k at 20° C.
	F	C and B	Vis.	Ppt.	Vis.	
Poly (Ethyl methacrylate)/ <i>n</i> -butanol	315.9	316.4	317.5	0.72	0.5	0.77
Poly (methyl methacrylate)/ <i>n</i> -butyl bromide	304.2	304.9	307.0	0.57	0.16	0.59
Poly (methyl methacrylate)/ isoamyl acetate	323.1	321.5	321.3	0.30	0.14	0.33

F = Flory (Pptn.) ;

C & B = Cornet and Ballegooijen ;
 k = Heat parameter.

Vis. = Viscometry ;

DISCUSSION

It may be seen that θ , obtained by the Flory-Huggins' plots and Cornet-Ballegooijen plots, agree within the limits of experimental error and also with the values obtained by viscometry. On the other hand the values of ψ obtained by precipitation were higher [than those from viscometry by a factor of 3 to 5. This is in accord with the trend reported by other workers⁵ also. This may be because (i) viscometric values may be in error (somewhat low) due to uncertainty of the exact values of the constants entering into their equations; and (ii) the precipitation values are for higher concentration regions and reflect perhaps the increase in ψ with increase in

concentration. For our systems also, the theoretical Flory-Huggins plots are much sharper and give lower values of the critical volume fraction v_2 compared with the experimental ones (Fig. 2). Taking these deviations to be due to concentration dependence of χ we have attempted at a rough estimation of the concentration effect using the Maron's theory according to which:

$$\chi = (\mu - \sigma^\circ v_1) = \mu - \sigma^\circ (1 - v_2)$$

where μ is the interaction parameter depending on concentration. To a first approximation;

$$\mu = \mu^\circ - \bar{\sigma}^\circ v_2; \quad \chi = (\mu^\circ - \sigma^\circ) + 2\sigma^\circ v_2$$

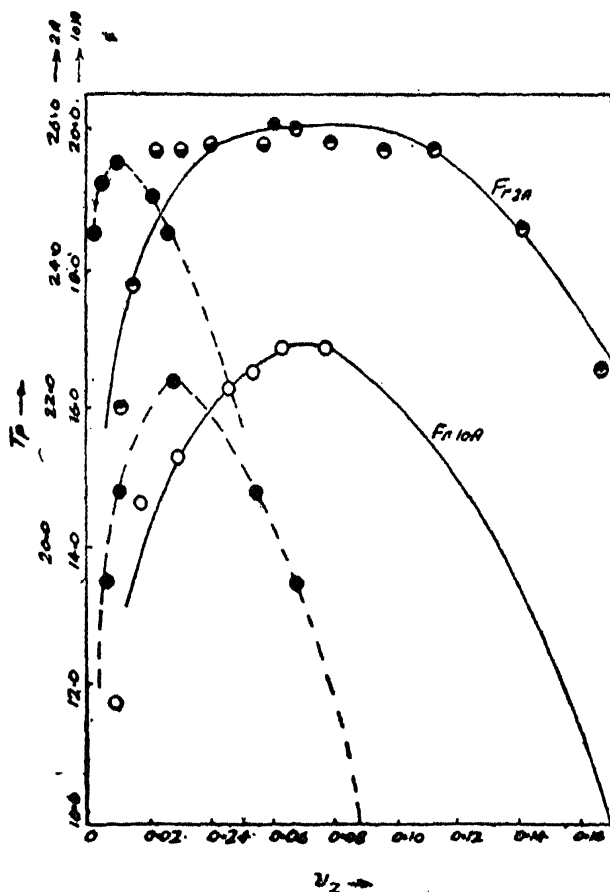


FIG. 2. Experimental and theoretical T_g versus v_2 plots for poly (M.M.A.)/*n*-butyl bromide (Fr. 2A, M , 11.560×10^5 ; Fr. 10A, 1.581×10^5 . Dotted lines refer to theoretical T_g versus v_2 curves.).

where μ° and σ° are constants for the system. Besides depending on concentration μ° will also depend on temperature and molecular weight. It may be assumed as a first approximation that the variation of $(\mu^\circ - \sigma^\circ)$ with temperature (T) and molecular weight of the fraction (M) is not very large. A tie line is drawn at a temperature T in the T_g versus v_2 curve for a polymer fraction of molecular weight M_1 and v_2' and v_2'' , the volume

fraction of polymer in the dilute and concentrated phases respectively are read off. In a similar way v_2' and v_2'' for the phases in equilibrium at the same temperature for another polymer fraction of molecular weight M_2 close to M_1 is found. Substitution in Maron's equation (neglecting the effective volume factors) results in simultaneous equations which may be solved for μ° and σ° . For *e.g.*,

$$\begin{aligned} RT \left[\ln v_1' + \left(1 - \frac{1}{x}\right) v_2' + (\mu - \sigma^\circ v_1') v_2'^2 \right] \\ = RT \left[\ln v_1'' + \left(1 - \frac{1}{x}\right) v_2'' + (\mu - \sigma^\circ v_1'') v_2''^2 \right] \end{aligned}$$

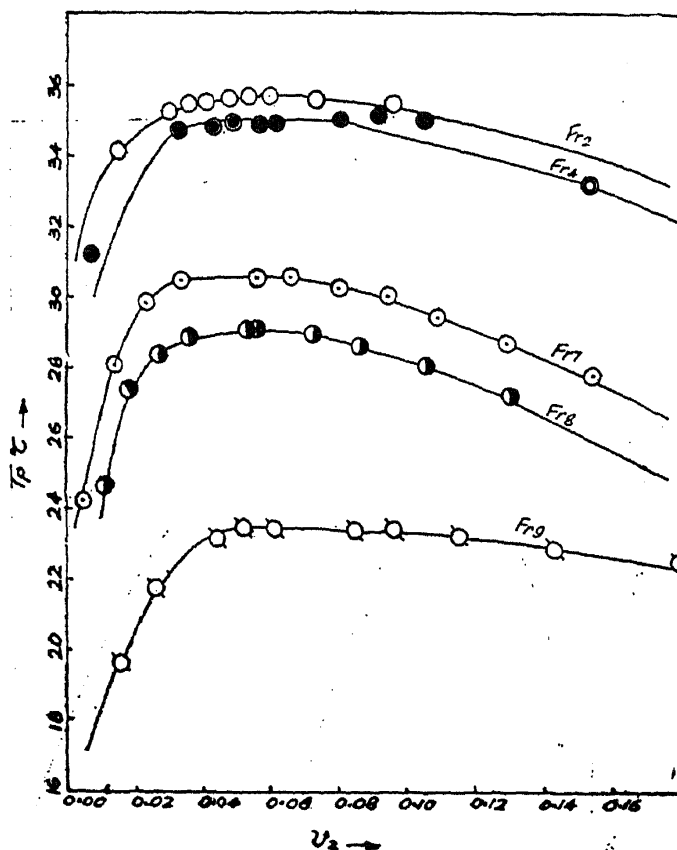


FIG. 3. T_g versus v_2 for poly (M.M.A.)/isoamyl acetate for fractions of different molecular weights (M_w) (Fr. 2 9.226×10^5 ; Fr. 4, 8.375×10^5 ; Fr. 7, 4.842×10^5 ; Fr. 8, 4.159×10^5 ; Fr. 9, 2.535×10^5).

for fraction M_1 is obtained. A similar equation for fraction M_2 may be obtained. Here v_1' and v_1'' are the volume fractions of the solvent in the dilute and concentrated phases. Alternatively, phases in equilibrium at two different temperatures of the same polymer fraction may be considered in a similar way, neglecting in this case the variation of $(\mu^\circ - \sigma^\circ)$ with a small variation in temperature. The values of μ° and σ° thus obtained are of the order of 0.6-0.8 and 0.1-0.3 respectively. This is of the same

order as the values reported in the literature for other systems,^{12, 18} e.g., polystyrene/cyclohexane where $\mu^\circ = 0.65-0.68$ and $\sigma^\circ = 0.15-0.18$. Thus we see that χ instead of being independent of volume fraction v_2 of the polymer is in fact related to it by:

$$\chi \sim 0.5 + 2\sigma^\circ v_2.$$

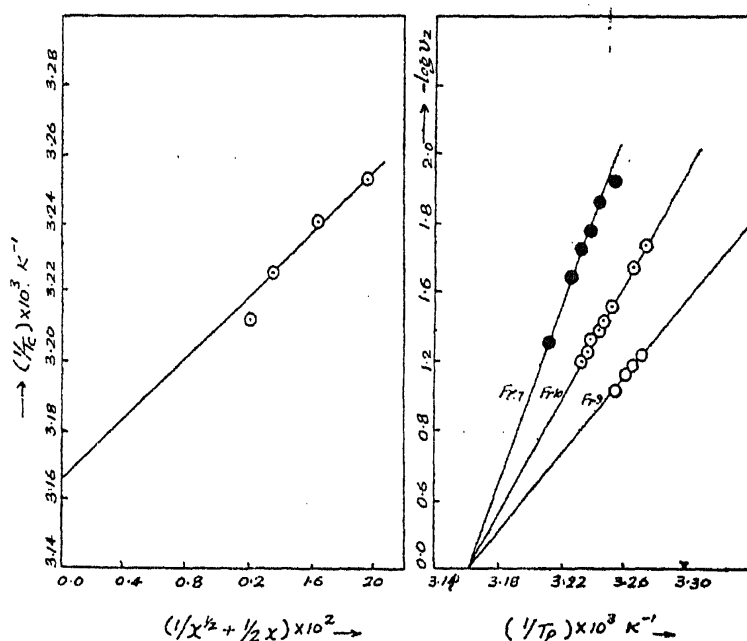


FIG. 4. $1/T_c$ versus $1/x^{1/2} + 1/2 x$ for poly (E.M. A.)/*n*-butanol.

FIG. 5. $-\log v_2$ versus $1/T_p$ for poly (E.M.A.)/*n*-butanol for different molecular weights (M_w) (Fr. 7, $M, 7.261 \times 10^5$; Fr. 10, 5.834×10^5 ; Fr. 9, 5.970×10^5).

This may explain the differences in χ (and ψ) values obtained by precipitation and viscometric techniques. In the former case the polymer concentration is high, of the order of $v_2 = 0.1$ at the critical point. In the latter case the parameters are estimated at $v_2 \rightarrow 0$. It follows that χ and hence ψ would be higher when obtained by precipitation as compared to the viscometric values.

ACKNOWLEDGEMENT

One of us (S. P. V.) is grateful to the U.G.C. for the award of J.R.F. during the tenure of which this investigation was carried out.

REFERENCES

1. Schultz, A. R. and Flory, P. J. *J. Amer. Chem. Soc.*, 1952, **74**, 4760.
2. Orofino, T. A. and Mickey, J. W. *J. Chem. Phys.*, 1963, **38**, 2512.

3. Flory, P. J. .. *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
4. *Polymer Hand Book*, Edited by Brandrup, J. and Immergut, E. H.
5. Fox, T. G. .. *Polymer*, 1962, 3, 111.
6. Tompa, H. .. *Polymer Solutions*, Butterworths Scientific Publications, 1956.
7. Krigbaum, W. R. and Wood, J. D. .. *J. Poly. Sci.*, 1964, Part A-2, 3075.
8. Stockmayer, W. H. .. *Die Makromol. Chem.*, 1960, 35, 54.
9. Maron, So .. *J. Poly. Sci.*, 1959, 38, 329.
10. Huggins, M. L. .. *Ibid.*, 1955, 16, 209.
11. ————— .. *J. Amer. Chem. Soc.*, 1964, 86, 3535.
12. Maron, S. H. and Nakajima, N. .. *J. Poly. Sci.*, 1961, 54, 587.
13. Elias, H. G. .. *Makromol. Chem.*, 1961, 50, 1.
14. ——— and Gruber, U. J. .. *J. Poly. Sci.*, 1963, B-1, 337.
15. Cornet, C. F. and Van Ballegooijen .. *Polymer*, 1966, 7, 293.
16. Chinai, S. N. and Samuels, R. J. .. *J. Poly. Sci.*, 1956, 19, 463.
17. Cohn. Ginsberg, E., Fox, T. G. and Mason, H. F. .. *Polymer*, 1962, 3, 97.
18. Holly .. *Polymer Letters*, 1964, 2, 541.
19. Vasudevan, Padma .. *Ph.D. Thesis*, Univ. of Madras, 1968.